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Physicochemical Properties of Quaternary Systems and Comparison of Different Geometrical Models

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ABSTRACT: Densities of the quaternary system consisting of {1-chlorobutane (1) + butylamine (2) + butylacetate (3) + isobutanol (4)}, related ternary systems of {1-chlorobutane (1) + butylamine (2) + butylacetate (3)}, (1-chlorobutane (1) + butylacetate (3) + isobutanol (4)}, and {butylamine (2) + butylacetate (3) + isobutanol (4)}, and binary systems of {1-chlorobutane (1) + butylacetate (3)} and {butylamine (2) + butylacetate (3)} were measured over the whole range of composition at 298.15 K and ambient pressure. Excess molar volumes, V_m^E, for the mixtures were derived and correlated as a function of mole fraction by using the Redlich–Kister and the Cibulka equations for binary and ternary mixtures, respectively. From the experimental data, partial molar volumes, $V_{m,i}$, and excess partial molar volumes, $V_{m,i}^E$, were also calculated for binary systems. The experimental results of the constituted binary mixtures have been used to test the applicability of the Prigogine–Flory–Paterson (PFP) theory. Values of densities and excess molar volumes, V_m^E, of other related binary and ternary systems were reported in our previous works. Some geometrical models which are the Kohler, Muggianu, Toop, Li, and a new model by Zhang as symmetric and asymmetric models have also been extended to estimate the physicochemical properties of quaternary systems based on the data of four subternary and six sub-binary systems. The experimental data were used to evaluate the nature and type of intermolecular interactions in multicomponent systems.

INTRODUCTION

The prediction of the thermodynamic properties of ternary, quaternary, and higher-order systems is important in calculating phase diagrams. The thermophysical properties are important to quantify the deviation from ideality of the thermodynamic functions of mixtures, which result essentially from molecular interactions. For industrial applications, it is of great importance to have access to reliable physicochemical properties of multicomponent systems. However, owing to the difficulties in measurements, data of high-order systems are very scarce, in comparison with the binary systems. Therefore, a proper model for estimating thermochemical and thermophysical properties of multicomponent systems with the properties of their lower order systems is very necessary. In recent years, some models have been developed for predicting the thermodynamic properties of quaternary and higher order systems from the properties of their lower order systems.[1,2] This paper is a part of an ongoing research effort to measure and characterize the thermophysical properties of mixtures containing organic solvents.[3−6] Mixtures of alcohols and primary amines are an interesting class of systems that exhibit very strong negative deviations from Raoult's law. It is very well-known that in the pure state the alcohol and the amine are associated by the formation of O−H···O and N−H···N hydrogen bonds, respectively. From vapor pressure and spectroscopic measurements it has been shown that the dimerization energy and the energy for the formation of higher polymers are nearly the same, for the amines and alcohols. Besides, esters are very important dipolar solvents of the best candidates that exist as dipolar associates in their pure liquid state, available with not only an aliphatic, aromatic, and even acrylic nature but also with a variety of general solvents. In this paper densities of the quaternary system consisting of {1-chlorobutane (1) + butylamine (2) + butylacetate (3) + isobutanol (4)}, ternary systems of {1-chlorobutane (1) + butylamine (2) + butylacetate (3)}, (1-chlorobutane (1) + butylacetate (3) + isobutanol (4)}, and {butylamine (2) + butylacetate (3) + isobutanol (4)}, and binary mixtures of {1-chlorobutane (1) + butylacetate (3)} and {butylamine (2) + butylacetate (3)} were measured over the whole range of composition at 298.15 K and ambient pressure. Excess molar volumes, V_m^E, for the mixtures were derived and correlated as a function of mole fraction by using the Redlich–Kister[7] and the Cibulka[8] equations for binary and ternary mixtures, respectively. Densities and excess molar volumes of other related ternary systems consist of {1-chlorobutane (1) + butylamine (2) + isobutanol (4)} and binary systems consist of {1-chlorobutane (1) + butylamine (2)}, {1-chlorobutane (1) + isobutanol (4)}, {butylamine (2) + isobutanol (4)}, and { butylacetate (3) + isobutanol (4)} was reported in previous works.[3,4] Some geometrical models have been used for predicting the thermodynamic properties of quaternary systems of {1-chlorobutane (1) + butylamine (2) + butylacetate (3) + isobutanol (4)}. Further, the experimental results of constitute binary mixtures have been used to test the applicability of the Prigogine–Flory–Paterson (PFP) theory.[9−11]

EXPERIMENTAL SECTION

Materials. 1-Chlorobutane, butylamine, butylacetate, and isobutanol were purchased from Merck with mass fractions higher than 99 % and used without further purifications. The purity of

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reagents were checked by comparing the measured densities and refractive indices at 298.15 K with those reported in the literature.[12] The results are in good agreement with values found in the literature and reported in Table 1. Compounds were stored in brown glass bottles and fractionally distilled immediately before use.

Table 1. Physical Properties of the Pure Compounds at T = 298.15 K

	ρ			
	$g\cdot cm^{-3}$		n_D	
compound	exp.	lit.[a]	exp.	lit.[a]
1-chlorobutane	0.88087	0.88090	1.3999	1.4001
butylamine	0.73458	0.73460	1.3983	1.3987
butylacetate	0.87624	0.87636	1.3920	1.3918
Isobutanol	0.79784	0.79780	1.3940	1.3939

[a] Reference 12.

Apparatus and Procedure. Samples of (10 to 12) g were prepared by filling glass vials with the liquids and weighing them on a Mettler AB204-N analytical balance, which measured of 0.0001 g. Vials were closed with a screw caps to ensure a secure seal and to prevent evaporation. The uncertainty in mole fractions was estimated to be less than 0.0001. The density of the pure compounds and their binary, ternary, and quaternary systems were measured with Anton Paar DMA 4500 operated in the static mode. The temperature was controlled by the self-contained Peltier system of the densimeter with an uncertainty of ± 0.01 K, and the uncertainty of the density measurement was estimated to be 0.00001 $g\cdot cm^{-3}$. The apparatus was calibrated once a day with dry air and double-distilled freshly degassed water. The densities of dry air and double-distilled freshly degassed water are reported as 0.001052 $g\cdot cm^{-3}$ and 0.997018 $g\cdot cm^{-3}$ at 298.15 K, respectively.[13] Airtight stoppered bottles were used for the preparation of the mixtures. The mass of the dry bottle was first determined. The less volatile component of the mixture was introduced in the bottle, and the total mass was recorded.

Table 2. Densities, ρ, Excess Molar Volumes, V_m^E, Partial Molar Volumes, $V_{m,i}$, and Excess Partial Molar Volumes, V_m^E for Binary Systems at T = 298.15 K

	ρ	V_m^E	$V_{m,1}$	$V_{m,2}$	V_1^E	V_2^E
x_1	$g\cdot cm^{-3}$	$cm^3\cdot mol^{-1}$	$cm^3\cdot mol^{-1}$	$cm^3\cdot mol^{-1}$	$cm^3\cdot mol^{-1}$	$cm^3\cdot mol^{-1}$
1-Chlorobutane (1) + Butylacetate (3)						
0.0000	0.87624	0.000	104.96	132.57	−0.137	0.000
0.0532	0.87648	−0.007	104.98	132.57	−0.125	0.000
0.1021	0.87671	−0.013	104.99	132.56	−0.113	−0.002
0.1521	0.87694	−0.018	105.00	132.56	−0.102	−0.004
0.2121	0.87722	−0.023	105.01	132.56	−0.090	−0.007
0.3076	0.87765	−0.030	105.03	132.55	−0.071	−0.015
0.3987	0.87807	−0.033	105.05	132.54	−0.055	−0.025
0.4521	0.87832	−0.034	105.05	132.53	−0.046	−0.032
0.4999	0.87854	−0.034	105.06	132.53	−0.039	−0.039
0.5598	0.87881	−0.033	105.07	132.52	−0.030	−0.048
0.6112	0.87904	−0.030	105.08	132.51	−0.024	−0.055
0.6986	0.87944	−0.026	105.09	132.50	−0.015	−0.068
0.8056	0.87993	−0.018	105.09	132.48	−0.006	−0.082
0.9023	0.88039	−0.009	105.10	132.47	−0.002	−0.091
1.0000	0.88087	0.000	105.10	132.47	0.000	−0.095
Butylamine (2) + Butylacetate (3)						
0.0000	0.87624	0.000	105.11	132.23	5.542	−0.340
0.0508	0.86898	0.270	104.52	132.24	4.957	−0.328
0.1112	0.86045	0.543	103.88	132.30	4.309	−0.269
0.1543	0.85433	0.722	103.44	132.37	3.877	−0.198
0.2098	0.84645	0.926	102.92	132.50	3.357	−0.070
0.3021	0.83334	1.198	102.15	132.80	2.583	0.234
0.4032	0.81903	1.387	101.43	133.27	1.860	0.701
0.4621	0.81062	1.456	101.06	133.61	1.498	1.041
0.5121	0.80352	1.479	100.79	133.94	1.223	1.370
0.5554	0.79737	1.475	100.58	134.25	1.009	1.687
0.6006	0.79095	1.447	100.38	134.62	0.808	2.051
0.7089	0.77552	1.286	99.99	135.63	0.422	3.069
0.7998	0.76260	1.029	99.76	136.66	0.197	4.096
0.9127	0.74664	0.541	99.60	138.19	0.037	5.621
1.0000	0.73458	0.000	99.57	139.58	0.000	7.012

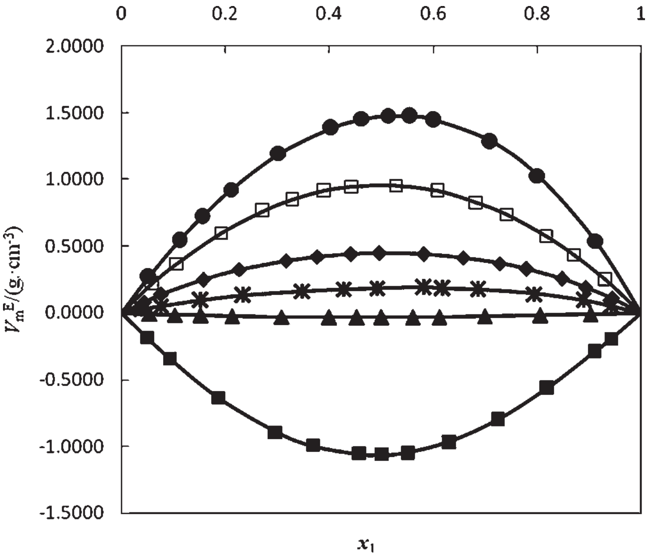

Figure 1. Excess molar volumes, V_m^E, at T = 298.15 K for the binary systems: ◆, 1-chlorobutane (1) + butylamine (2) from ref 3; ▲, 1-chlorobutane (1) + butylacetate (3); ∗, 1-chlorobutane (1) + isobutanol (4) from ref 3; ●, butylamine (2) + butylacetate (3); ■, butylamine (2) + isobutanol (4) from ref 3; and □, butylacetate (3) + isobutanol (4) from ref 4. x_1 is the mole fraction of the first component in each binary system. The solid line was calculated with the Redlich–Kister equation.

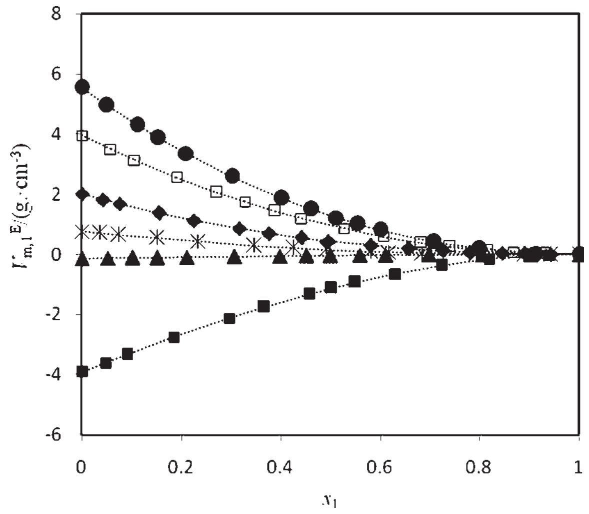

Figure 2. Excess partial molar volumes, $V_{m,1'}^E$, at T = 298.15 K for the binary systems: ◆, 1-chlorobutane (1) + butylamine (2) from ref 3; ▲, 1-chlorobutane (1) + butylacetate (3); ∗, 1-chlorobutane (1) + isobutanol (4) from ref 3; ●, butylamine (2) + butylacetate (3); ■, butylamine (2) + isobutanol (4) from ref 3; and □, butylacetate (3) + isobutanol (4) from ref 4. x_1 is the mole fraction of the first component in each binary system.

Subsequently, the other components were introduced, and the mass of bottle along with the other components was determined. Mixtures were immediately used after being well-mixed by shaking.

RESULTS AND DISCUSSION

Binary Systems. The excess molar volume for all mixtures was calculated from density results at 298.15 K and at ambient pressure using the following equation:[14]

$$V_m^E = \sum_{i=1}^{N} x_i M_i(\rho^{-1} - \rho_i^{-1}) \tag{1}$$

where ρ is the density of the mixture, ρ_i is the density of pure component, x_i is the mole fraction, M_i is the molar mass of component i, and N stands for the number of components in the mixtures. The excess molar volumes are estimated to ± 0.001 cm^3·mol^{-1}. The corresponding V_m^E values of binary mixtures of {1-chlorobutane (1) + butylacetate (3)} and {butylamine (2) + butylacetate (3)} at 298.15 K are presented in Table 2 and plotted against mole fraction x, in Figure 1. The partial molar volumes, $V_{m,i}$, in these mixtures were calculated over the whole composition range using eq 2.[14]

$$V_{m,i} = V_m^E + V_{m,i}{}^* + (1 - x_i)(\partial V_m^E/\partial x_i)_{T,P} \tag{2}$$

where $V_{m,i}{}^*$ is the pure molar volume of component i. The excess partial molar volumes $V_1^E = (V_{m,1} - V_{m,1}^0)$ and $V_2^E = (V_{m,2} - V_{m,2}^0)$ from V_m^E and the molar volumes of the pure components are also calculated. The values of partial molar volumes and the excess partial molar volumes are presented in Table 2, and the latter was plotted against mole fraction in Figures 2 and 3.

The values of densities, excess molar volumes, and excess partial molar volumes for other related binary systems were reported in previous works.[3,4] Experimental results for binary systems were fitted by the least-squares method with all points weighted equally to the Redlich–Kister polynomial equation:[7]

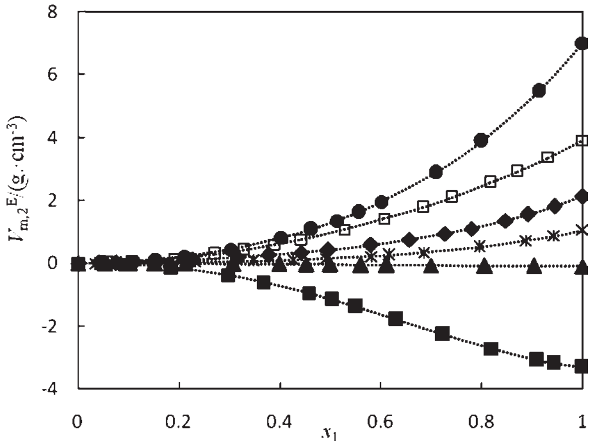

Figure 3. Excess partial molar volumes, $V_{m,2}^E$, at T = 298.15 K for the binary systems: ◆, 1-chlorobutane (1) + butylamine (2) from ref 3; ▲, 1-chlorobutane (1) + butylacetate (3); ∗, 1-chlorobutane (1) + isobutanol (4) from ref 3; ●, butylamine (2) + butylacetate (3); ■, butylamine (2) + isobutanol (4) from ref 3; and □, butylacetate (3) + isobutanol (4) from ref 4. x_1 is the mole fraction of the first component in each binary system.

$$V_m^E = x(1 - x)\sum_{k=0}^{N} A_i(1 - 2x)^k \tag{3}$$

where x is the mole fraction of solvent, A_i are adjustable parameters obtained by least-squares method, and N is the degree of the polynomials. For none of the systems does the precision warrant the use of more than three parameters. In each case, the optimum number of coefficients was ascertained from an examination of the variation of the standard deviation σ, with

$$\sigma = \left[\sum \frac{(V^{E}_{\mathrm{m,\,exp}} - V^{E}_{\mathrm{m,\,cal}})^2}{n - p}\right]^{1/2} \tag{4}$$

where $V^{E}_{\mathrm{m,exp}}$ and $V^{E}_{\mathrm{m,cal}}$ are the experimental and calculated values of the excess molar volumes, respectively, and n and p are the number of experimental points and number of parameters retained in the respective equations. The coefficients A_i of eq 2 were obtained by the method of least-squares are given in Table 3 together with corresponding standard deviations.

V^{E}_{m} is the resulting contribution from several opposing effects. These effects may be divided arbitrarily into three types, namely, physical, chemical, and structural. Physical contributions, that is, nonspecific interactions between the real species present in the mixture, contribute a positive term to V^{E}_{m}. The chemical or specific intermolecular interactions result in a volume decrease, and these include charge-transfer type forces and other complex-forming interactions. This effect contributes with negative values to V^{E}_{m}. The structural contributions are mostly negative and arise from several effects, especially from interstitial accommodation and changes of free volume.

PFP Theory. The PFP theory has been commonly employed to analyze thermodynamic function for binary systems. This theory has been used to interpreting the results of measurements of the excess properties of a number of binary systems formed by molecular species which differ in size and shape.

According to the PFP theory, V^{E}_{m} calculations include three contributions: (i) interactional, which is proportional to the (χ_{12}) parameters; (ii) the free volume contribution which arises from the dependence of the reduced volume upon the reduced temperature as a result of the difference between the degree of expansion of the two components, and (iii) the (P^*) contribution, which depends both on the differences of internal pressures and differences of reduced volumes of the components. The V^{E}_{m} was calculated by means of the PFP theory using the following equation with the three contributions.[9−11]

$$\begin{aligned} V^{E}/(x_1V_1^* + x_2V_2^*) &= \frac{(\tilde{V}^{1/3} - 1)\tilde{V}^{2/3}\Psi_1\theta_2\chi_{12}}{((4/3)\tilde{V}^{-1/3} - 1)/P_1^*} \\ &\quad - \frac{(\tilde{V}_1 - \tilde{V}_2)^2((14/9)\tilde{V}^{-1/3} - 1)\Psi_1\Psi_2}{((4/3)\tilde{V}^{-1/3} - 1)\tilde{V}} \\ &\quad + \frac{(\tilde{V}_1 - \tilde{V}_2)(P_1^* - P_2^*)\Psi_1\Psi_2}{P_1^*\Psi_2 + P_2^*\Psi_1} \end{aligned} \tag{5}$$

The $\tilde{V}$ of the solution is obtained through Flory's theory. The characteristic parameters V^* and P^* are obtained from thermal expansion coefficient, α_i,[12] and isothermal compressibility, β_T.[12] The thermal expansion coefficient, α_i, is used to calculate the reduced volume by the equation:

$$\tilde{V}_i = (1 + ((4/3)\alpha_i T)/(1 + \alpha_i T))^3 \tag{6}$$

Here, the molecular contact energy fraction is calculated by:

$$\Psi_1 = \varphi_1 P_1^*/(\varphi_1 P_1^* + \varphi_2 P_2^*) \tag{7}$$

with the hard-core volume fractions defined by:[15]

$$\varphi_1 = x_1V_1^*/(x_1V_1^* + x_2V_2^*) \tag{8}$$

The values of pure parameters for the pure liquid components and the mixture are obtained by Flory theory. The parameters for the pure liquid components derived using Flory theory are in Table 4.

Table 3. Coefficients of the Redlich−Kister Equation, A_i, and Standard Deviations, $\sigma(V^{E}_{m})$ for Binary Systems at T = 298.15 K

	A_i			$\sigma(V^{E}_{m})$
	g·cm^{-3}			
system	A_0	A_1	A_2	g·cm^{-3}
1-chlorobutane (1) + butylamine (2)[a]	1.797	−0.061	0.278	0.0009
1-chlorobutane (1) + butylacetate (3)	−0.134	−0.021	0.018	0.0003
1-chlorobutane (1) + isobutanol (4)[a]	0.746	−0.136	0.16	0.0008
butylamine (2) + butylacetate (3)	5.882	−0.735	0.395	0.005
butylamine (2) + isobutanol (4)[a]	−4.257	−0.31	0.644	0.006
butylacetate (3) + isobutanol (4)[b]	3.827	0.019	0.106	0.0004

[a] Reference 3. [b] Reference 4.

Table 4. Parameters of Pure Components Used in Flory Theory: Reduction Parameters for Pressure, P^*, Molar Hard Core Volumes, V^*, and Temperature, T^*, at T = 298.15 K

	P^*	V^*	T^*
component	J·cm^{-3}	cm^3·mol^{-1}	K
1-chlorobutane	493.651	81.618	4749.64
butylamine	586.035	76.079	4548.75
butylacetate	513.001	101.313	5045.43
isobutanol[a]	436.253	70.997	5296.04

[a] Reference 3.

The values of thermal expansion coefficient, α_i, and isothermal compressibility, β_T, for the pure components are obtained from the literature. To obtain V^{E}_{m}, it is necessary to find the interactional parameter, χ_{12}, which was obtained by fitting the theory to experimental values of V^{E}_{m} for each one of the binary systems. Table 5 presents the calculated equimolar values of the three contributions to V^{E}_{m} according to the equation, together with the interactional parameter, χ_{12}. An analysis of each of the three contributions to V^{E}_{m} shows that the interactional contribution is positive for the most of binary mixtures except for the system consisting of {butylamine (2) + isobutanol (4)} and seems to be the most important to explain the V^{E}_{m} behavior for system studied. The free volume effect is negative, and it seems to have little significance for the system studied.

Ternary Systems. Excess molar volumes for ternary mixtures of {1-chlorobutane (1) + butylamine (2) + butylacetate (3)}, (1-chlorobutane (1) + butylacetate (3) + isobutanol (4)}, and {butylamine (2) + butylacetate (3) + isobutanol (4)} at 298.15 K were calculated using eq 1, and the results are listed in Table 6 and graphically shown in Figures 4 to 6.

The excess molar volumes for the ternary systems were correlated using the Cibulka equation:[8]

$$\Delta Q_{123} = \Delta Q_{\mathrm{bin}} + x_1x_2x_3\Delta_{123} \tag{9}$$

and

$$\Delta Q_{\mathrm{bin}} = \sum_{i=1}^{3}\sum_{j>i}^{3} \Delta Q_{ij} \tag{10}$$

Table 5. Calculated Values of Contributions of the PFP Theory: Interactional Parameters, $\chi_{1,2}$, Interactional and Free Volume, and Reduction Parameters for Pressure, P^* for Binary Mixtures at T = 298.15 K

	$\chi_{1,2}$			
system	$J \cdot cm^{-3}$	interactional	free volume	P^*
1-chlorobutane (1) + butylamine (2)[a]	20.7	0.4104	−0.0129	538.146
1-chlorobutane (1) + butylacetate (3)	0.6	0.0114	−0.0228	504.489
1-chlorobutane (1) + isobutanol (4)[a]	8.4	0.1384	−0.0560	465.807
butylamine (2) + butylacetate (3)	86.6	1.3958	−0.7222	525.631
butylamine (2) + isobutanol (4)[a]	−70.2	−1.0744	−27.7956	483.734
butylacetate (3) + isobutanol (4)[b]	52.5	0.9115	−0.0105	427.134

[a] Reference 3. [b] Reference 4.

Table 6. Densities, ρ, and Excess Molar Volumes, V_m^E, for Ternary Systems at T = 298.15 K

		ρ	V_m^E
x_1	x_2	$g \cdot cm^{-3}$	$cm^3 \cdot mol^{-1}$
1-Chlorobutane (1) + Butylamine (2) + Butylacetate (3)			
0.0539	0.0533	0.86900	0.243
0.0589	0.1756	0.85189	0.704
0.0561	0.3442	0.82811	1.126
0.0567	0.5445	0.79948	1.280
0.0508	0.8665	0.75255	0.651
0.0564	0.6048	0.79077	1.251
0.0589	0.3798	0.82309	1.173
0.0679	0.2121	0.84685	0.798
0.0759	0.0658	0.86739	0.281
0.1084	0.5533	0.79877	1.094
0.1456	0.0327	0.87241	0.113
0.1469	0.1749	0.85279	0.567
0.1519	0.3332	0.83070	0.867
0.1233	0.7649	0.76783	0.703
0.2508	0.1750	0.85357	0.436
0.2289	0.3457	0.82957	0.718
0.2087	0.5462	0.80049	0.798
0.2019	0.6672	0.78253	0.674
0.2169	0.4439	0.81545	0.798
0.2372	0.2587	0.84187	0.600
0.3074	0.5463	0.80062	0.584
0.3743	0.4357	0.81706	0.518
0.3620	0.3511	0.82944	0.507
0.4336	0.3852	0.82445	0.447
0.4749	0.0329	0.87373	0.073
0.4592	0.1752	0.85455	0.267
0.4198	0.3456	0.83030	0.441
0.4203	0.4290	0.81795	0.469
0.4411	0.2556	0.84326	0.360
0.4920	0.1004	0.86484	0.166
0.5007	0.2974	0.83725	0.357
0.5497	0.1758	0.85464	0.234
0.5363	0.3219	0.83350	0.365
0.5786	0.1259	0.86160	0.179
0.6312	0.1782	0.85428	0.229
0.6379	0.2358	0.84581	0.294
0.7134	0.1755	0.85438	0.252
0.8815	0.0316	0.87510	0.120
0.8657	0.0661	0.86995	0.184
0.9176	0.0329	0.87484	0.151
1-Chlorobutane (1) + Butylacetate (3) + Isobutanol (4)			
0.0526	0.0525	0.80663	0.203
0.0484	0.1756	0.81598	0.522
0.0552	0.3442	0.82980	0.761
0.0585	0.5494	0.84605	0.777
0.0756	0.8665	0.87210	0.167
0.0699	0.6048	0.85135	0.699
0.0601	0.3798	0.83303	0.777
0.0584	0.2121	0.81975	0.584
0.0547	0.0658	0.80787	0.243
0.1313	0.5533	0.85280	0.582
0.1028	0.0327	0.80949	0.154
0.1247	0.1749	0.82278	0.460
0.1535	0.3332	0.83777	0.585
0.1762	0.7649	0.87265	0.122
0.2218	0.1750	0.83130	0.389
0.2412	0.3457	0.84638	0.450
0.2612	0.5462	0.86328	0.291
0.2770	0.6672	0.87348	0.077
0.2495	0.4439	0.85460	0.404
0.2293	0.2587	0.83858	0.446
0.4002	0.5463	0.87432	0.040
0.4555	0.4357	0.87065	0.088
0.4048	0.3511	0.86039	0.221
0.5164	0.3852	0.87170	0.062
0.3838	0.0329	0.83335	0.216
0.4431	0.1752	0.84989	0.246
0.4784	0.3456	0.86585	0.137
0.5183	0.4290	0.87495	0.020
0.4624	0.2556	0.85777	0.208
0.4390	0.1004	0.84349	0.246
0.5630	0.2974	0.86890	0.086
0.5525	0.1758	0.85879	0.176

Table 6. Continued

x_1	x_2	ρ $\mathrm{g\cdot cm^{-3}}$	V_m^E $\mathrm{cm^3\cdot mol^{-1}}$
0.6282	0.3219	0.87564	0.012
0.5545	0.1259	0.85494	0.201
0.6605	0.1782	0.86755	0.098
0.7150	0.2358	0.87604	0.014
0.7740	0.1755	0.87615	0.021
0.8649	0.0316	0.87210	0.115
0.8835	0.0661	0.87646	0.045
0.9176	0.0329	0.87484	0.049
Butylamine (2) + Butylacetate (3) + Isobutanol (4)			
0.0579	0.0522	0.79999	−0.034
0.0605	0.1734	0.80945	0.318
0.0689	0.3392	0.82221	0.594
0.0729	0.5410	0.83787	0.675
0.0938	0.8495	0.86057	0.298
0.0868	0.5938	0.84128	0.642
0.0749	0.3738	0.82468	0.617
0.0728	0.2089	0.81179	0.362
0.0682	0.0649	0.80062	−0.028
0.1606	0.5347	0.83276	0.629
0.1267	0.0318	0.79583	−0.348
0.1528	0.1693	0.80541	0.044
0.1867	0.3201	0.81528	0.353
0.2130	0.7307	0.84365	0.716
0.2652	0.1653	0.79962	−0.166
0.2869	0.3249	0.80999	0.322
0.3092	0.5108	0.82151	0.772
0.3266	0.6215	0.82761	1.012
0.2962	0.4163	0.81587	0.555
0.2736	0.2439	0.80493	0.088
0.4579	0.4937	0.80868	1.230
0.5143	0.3886	0.79750	1.051
0.4626	0.3170	0.79730	0.550
0.5748	0.3387	0.78922	1.077
0.4409	0.0299	0.77954	−0.886
0.5018	0.1568	0.78398	−0.142
0.5373	0.3066	0.79063	0.741
0.5766	0.3770	0.79119	1.301
0.5212	0.2276	0.78707	0.278
0.4976	0.0899	0.77986	−0.520
0.6198	0.2587	0.78060	0.811
0.6098	0.1533	0.77535	0.090
0.6814	0.2758	0.77559	1.272
0.6117	0.1097	0.77256	−0.196
0.7112	0.1516	0.76638	0.465
0.7605	0.1982	0.76361	1.167
0.8126	0.1455	0.75568	1.036
0.8902	0.0257	0.74392	0.061
0.9057	0.0535	0.74227	0.629
0.9338	0.0264	0.73904	0.384

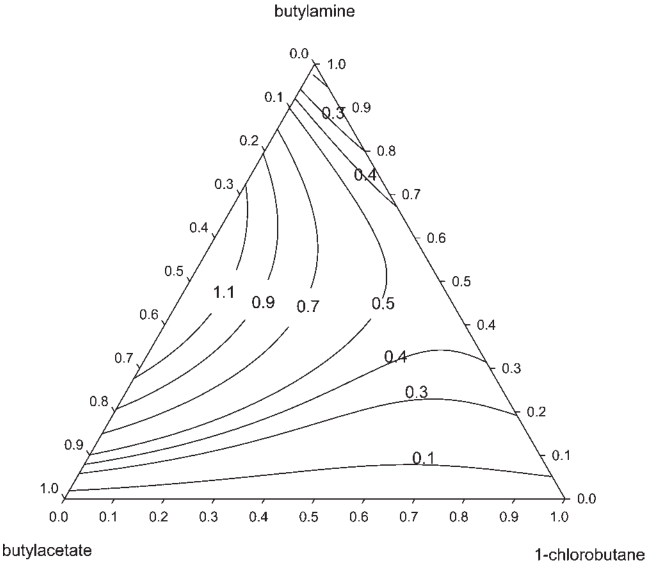

Figure 4. Isolines at constant excess molar volume, V_m^E, for ternary mixtures of 1-chlorobutane (1) + butylamine (2) + butylacetate (3) correlated by the Cibulka equation.

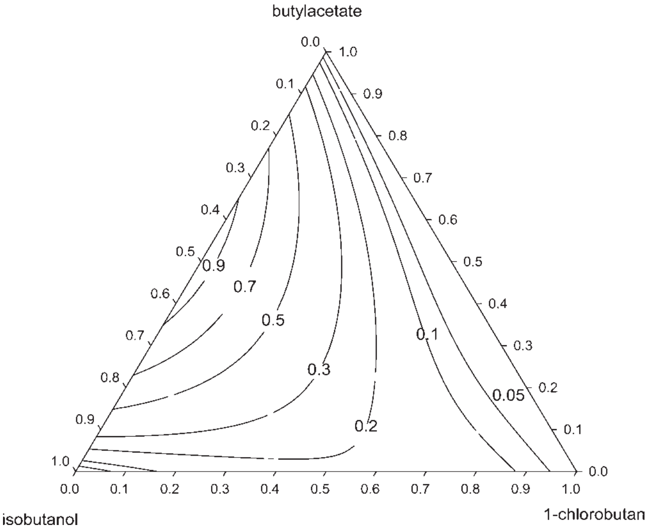

Figure 5. Isolines at constant excess molar volume, V_m^E, for ternary mixtures of 1-chlorobutane (1) + butylacetate (3) + isobutanol (4) correlated by the Cibulka equation.

where ΔQ_{123} refers to V_m^E for the ternary system and $x_3 = 1 - x_1 - x_2$. ΔQ_{ij} in eq 10 is the binary contribution of each $i-j$ pair to the V_m^E given by eq 3 with the parameters of A_i, reported in Table 3. The ternary contribution term Δ_{123} was correlated using the expression suggested by Cibulka:

$$\Delta_{123} = B_0 + B_1 x_1 + B_2 x_2 \tag{11}$$

The ternary parameters, B_0, B_1, and B_2, were determined with the optimization algorithm similar to that for the binary parameters. The fitting parameters and the corresponding standard deviations are given in Table 7. The corresponding value of the ternary system of {1-chlorobutane (1) + butylamine (2) + isobutanol (4)} was reported in a previous work.[3]

Quaternary Systems. Excess molar volumes for quaternary systems of {1-chlorobutane (1) + butylamine (2) + butylacetate (3) + isobutanol (4)} at 298.15 K were calculated using eq 1, and the results are listed in Table 8.

It has been stated that the symmetrical models can be applied to the quaternary system. Among them, the most widely used is the Kohler and Muggianu models.[2] They have given a complete summary in which it is stated that the properties of a quaternary system can be expressed as a combination of the properties of all binary systems with an assigned probability weight:

$$Y_m^E = W_{12}Y^E_{m,12} + W_{13}Y^E_{m,13} + W_{14}Y^E_{m,14} + W_{23}Y^E_{m,23} + W_{24}Y^E_{m,24} + W_{34}Y^E_{m,34} \tag{12}$$

where Y_m^E and W_{ij} represents the excess molar function and weight probability of each corresponding binary composition point which can be calculated in terms of the following form:

$$W_{ij} = \frac{x_i x_i}{X_i X_j} \tag{13}$$

where x_i and x_j represent the molar fraction of components i and j in a quaternary system; X_i and X_j are the selected binary compositions which are different for various kinds of geometric models. Combining eqs 1, 12, and 13 the excess properties of a quaternary system should be

$$\begin{aligned} Y_m^E = {} & x_1x_2\sum_{k=0}^{n} A_{12}^k(2X_{1(12)}-1)^k \\ & + x_1x_3\sum_{k=0}^{n} A_{13}^k(2X_{1(13)}-1)^k + x_1x_4\sum_{k=0}^{n} A_{14}^k(2X_{1(14)}-1)^k \\ & + x_2x_3\sum_{k=0}^{n} A_{23}^k(2X_{2(23)}-1)^k + x_2x_4\sum_{k=0}^{n} A_{24}^k(2X_{2(24)}-1)^k \\ & + x_3x_4\sum_{k=0}^{n} A_{34}^k(2X_{3(34)}-1)^k \end{aligned} \tag{14}$$

X_i and X_j are different in different models:

Kohler model:

$$X_{i(ij)} = \frac{x_i}{x_i + x_j} \tag{15}$$

Muggianu model:

$$X_{i(ij)} = x_i + \frac{1 - x_i - x_j}{2} \tag{16}$$

According to eqs 15 and 16, the following formulas can be obtained:

Kohler model:

$$\begin{aligned} Y_m^E = {} & x_1x_2\sum_{k=0}^{n} A_{12}^k\left(\frac{x_1-x_2}{x_1+x_2}\right)^k + x_1x_3\sum_{k=0}^{n} A_{13}^k\left(\frac{x_1-x_3}{x_1+x_3}\right)^k \\ & + x_1x_4\sum_{k=0}^{n} A_{14}^k\left(\frac{x_1-x_4}{x_1+x_4}\right)^k + x_2x_3\sum_{k=0}^{n} A_{23}^k\left(\frac{x_2-x_3}{x_2+x_3}\right)^k \\ & + x_2x_4\sum_{k=0}^{n} A_{24}^k\left(\frac{x_2-x_4}{x_2+x_4}\right)^k + x_3x_4\sum_{k=0}^{n} A_{34}^k\left(\frac{x_3-x_4}{x_3+x_4}\right)^k \end{aligned} \tag{17}$$

Muggianu model:

$$\begin{aligned} Y_m^E = {} & x_1x_2\sum_{k=0}^{n} A_{12}^k\left(\frac{x_1-x_2}{x_1+x_2}\right)^k + x_1x_3\sum_{k=0}^{n} A_{13}^k\left(\frac{x_1-x_3}{x_1+x_3}\right)^k \\ & + x_1x_4\sum_{k=0}^{n} A_{14}^k\left(\frac{x_1-x_4}{x_1+x_4}\right)^k + x_2x_3\sum_{k=0}^{n} A_{23}^k\left(\frac{x_2-x_3}{x_2+x_3}\right)^k \\ & + x_2x_4\sum_{k=0}^{n} A_{24}^k\left(\frac{x_2-x_4}{x_2+x_4}\right)^k + x_3x_4\sum_{k=0}^{n} A_{34}^k\left(\frac{x_3-x_4}{x_3+x_4}\right)^k \end{aligned} \tag{18}$$

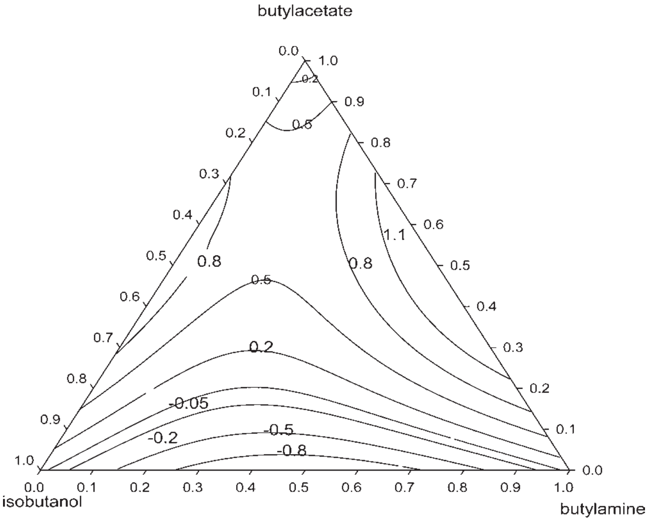

Figure 6. Isolines at constant excess molar volume, V_m^E, for ternary mixtures of butylamine (2) + butylacetate (3) + isobutanol (4) correlated by the Cibulka equation.

Table 7. Ternary Coefficients of the Cibulka Equation, B_i, and Standard Deviations, $\sigma(V_m^E)$, at T = 298.15 K

	B_i/ g·cm^{-3}			$\sigma(V_m^E)$
system	B_0	B_1	B_2	g·cm^{-3}
1-chlorobutane (1) + butylamine (2) + butylacetate (3)	−7.238	−0.179	−0.128	0.030
1-chlorobutane (1) + butylamine (2) + isobutanol (4)[a]	−30.521	−28.202	63.738	0.020
1-chlorobutane (1) + butylacetate (3) + isobutanol (4)	−4.529	0.719	−0.940	0.008
butylamine (2) + butylacetate (3) + isobutanol (4)	−8.430	22.102	−14.863	0.097

[a] Reference 3.

Table 8. Densities, ρ, and Excess Molar Volumes, V_m^E, for Quaternary Systems of 1-Chlorobutane (1) + Butylamine (2) + Butylacetate (3) + Isobutanol (4) at T = 298.15 K

			ρ	V_m^E
x_1	x_2	x_3	$g\cdot cm^{-3}$	$cm^3\cdot mol^{-1}$
0.0557	0.0567	0.0555	0.80491	0.033
0.0575	0.0610	0.2279	0.81790	0.512
0.0613	0.0629	0.4237	0.83291	0.784
0.0656	0.0697	0.6230	0.84800	0.762
0.0615	0.0596	0.8289	0.86411	0.423
0.0448	0.2708	0.0357	0.79279	−0.574
0.0488	0.2651	0.2268	0.80645	0.266
0.0595	0.2414	0.4559	0.82473	0.837
0.0654	0.2499	0.6403	0.83775	0.992
0.0535	0.4689	0.2346	0.79367	0.496
0.0594	0.4524	0.4387	0.80865	1.230
0.0478	0.6547	0.0415	0.76728	−0.306
0.0521	0.6511	0.2340	0.77936	0.983
0.0474	0.8569	0.0487	0.75086	0.363
0.1091	0.0559	0.0383	0.80811	0.012
0.1129	0.0632	0.2456	0.82368	0.535
0.1053	0.0538	0.4536	0.83924	0.757
0.1046	0.0539	0.6602	0.85493	0.635
0.0947	0.2632	0.0477	0.79779	−0.414
0.1124	0.2594	0.2376	0.81228	0.361
0.1128	0.2405	0.4442	0.82795	0.808
0.1020	0.2543	0.5969	0.83708	0.959
0.1153	0.4441	0.0390	0.78739	−0.448
0.1239	0.4485	0.2447	0.80064	0.624
0.1082	0.4525	0.3961	0.80918	1.148
0.2065	0.0576	0.0454	0.81658	0.100
0.2419	0.0661	0.2410	0.83354	0.505
0.2030	0.0517	0.4532	0.84718	0.644
0.2066	0.0506	0.6451	0.86219	0.441
0.2050	0.2426	0.0436	0.80690	−0.223
0.2028	0.2465	0.2506	0.82067	0.464
0.2084	0.2480	0.4478	0.83477	0.801
0.1975	0.4487	0.0514	0.79339	−0.154
0.1953	0.4550	0.2467	0.80513	0.763
0.2055	0.6442	0.0498	0.77864	0.264
0.2949	0.0511	0.0470	0.82409	0.182
0.3059	0.0581	0.2445	0.83925	0.506
0.3073	0.0499	0.4541	0.85561	0.519
0.2940	0.0505	0.6078	0.86628	0.332
0.2929	0.2523	0.0505	0.81319	−0.056
0.3295	0.4105	0.2271	0.81634	0.784
0.3055	0.4473	0.0464	0.80037	0.092
0.3003	0.4461	0.2014	0.80994	0.743
0.4073	0.0500	0.0446	0.83274	0.256
0.3968	0.0537	0.2496	0.84693	0.493
0.3946	0.0505	0.4459	0.86173	0.422
0.3920	0.2553	0.0464	0.81977	0.091
0.4125	0.2487	0.2475	0.83539	0.595
0.3977	0.4491	0.0540	0.80680	0.350
0.5075	0.0508	0.0431	0.84023	0.320
0.4976	0.0546	0.2453	0.85423	0.465
0.5038	0.0554	0.3925	0.86576	0.367
0.4987	0.2501	0.0425	0.82734	0.241
0.5014	0.2442	0.1262	0.83362	0.443
0.6112	0.0515	0.2491	0.86329	0.416
0.6021	0.0555	0.2877	0.86527	0.394
0.5354	0.0478	0.0434	0.84252	0.342
0.6032	0.2545	0.0478	0.83470	0.395
0.6951	0.0540	0.0504	0.85465	0.416
0.6983	0.2008	0.0451	0.84503	0.431
0.7039	0.0552	0.1944	0.86596	0.406
0.7962	0.0521	0.0526	0.86258	0.424
0.7946	0.1067	0.0499	0.85880	0.422

In new generation geometric model by Zhang et al.,[2] $X_{i(ij)}$ in eq 14 is expressed in terms of the following expression

$$X_{i(ij)} = x_i + \sum_{\substack{k=1 \\ k \neq i,j}}^{4} \xi_{i(ij)}^{k} x_k \tag{19}$$

where $\xi_{i(ij)}^{k}$ is the "similarity coefficient", which is defined as:

$$\xi_{i(ij)}^{k} = \frac{\eta(ij, ik)}{\eta(ij, ik) + \eta(ji, jk)} \tag{20}$$

Here η is called the "deviation sum of squares" and can be calculated as follows:

$$\eta(ij, ik) = \int_0^1 (Y_{m,ij}^E - Y_{m,ik}^E)^2 dX_i \tag{21}$$

The integration process of eq 21 makes the calculation a little bit inconvenient. If the relations between the "similarity coefficient" and the parameters of the binary $R-K$ type polynomial are known, the integration can be completely avoided, and instead, the algebraic operation can be carried out. Chou et al.[2] have dealt with the case of "$n = 2$" and "$n = 3$" (n is the highest order in eq 2).

Recently, a general relation has been derived, in principle, which allows us to go to any high order term:[2]

$$\eta(ij, ik) = \sum_{l=0}^{n} \frac{1}{2(2l+1)(2l+3)(2l+5)} (A_{ij}^{l} - A_{ik}^{l})^2 + \sum_{l=0}^{n} \sum_{m \rangle l} \frac{1}{(l+m+1)(l+m+3)(l+m+5)} (A_{ij}^{l} - A_{ik}^{l})(A_{ij}^{m} - A_{ik}^{m}) \tag{22}$$

Please note that, in eq 22, the second term is not equal to "0" only if "$l + m$" is an even number. Substituting eq 22 into eq 20, the similarity coefficients can be obtained. It should be pointed out that the parameters appearing in above equation observe the following regulation

$$A_{ij}^{k} = (-1)^k A_{ji}^{k}$$

When the similarity coefficients are obtained, properties of the quaternary system can be estimated according to eqs 14 and 19.

Table 9. Standard Deviation, $S/(V_m^E)$, in the Prediction of V_m^E, with Different Models for the Quaternary Mixtures at T = 298.15 K

model	$S/(V_m^E)$
Kohler	0.04
Muggianu	0.02
Zhang	0.01
Toop	0.03
Li	0.02

The excess properties of quaternary system have also been calculated by Toop and Li[2] models from the ternary data as follows:[1]

Toop model:

$$Y_m^E = \frac{x_2}{1-x_1}Y_{12}^m + \frac{x_3}{1-x_1}Y_{13}^m + \frac{x_4}{1-x_1}Y_{14}^m + (1-x_1)^2 Y_{234}^m \quad (23)$$

Li model:

$$Y_m^E = (1-x_4)^2 Y_{m,123}^m + (1-x_3)^2 Y_{m,124}^m + (1-x_2)^2 Y_{m,134}^m + (1-x_1)^2 Y_{m,234}^m \quad (24)$$

In a word, the thermodynamic properties of the quaternary l + 2 + 3 + 4 system can be evaluated either from one of its six binary subsystems 1 + 2, 1 + 3, 1 + 4, 2 + 3, 2 + 4, and 3 + 4 by eqs 17 to 22 or from one of its binary systems 1 + 2, 1 + 3, or 1 + 4, as well as the ternary system 2 + 3 + 4 by eq 23, or from one of its ternary systems l + 2 + 3, 1 + 2 + 4, 1 + 3 + 4, and 2 + 3 + 4 by eq 24.

Standard deviations presented in Table 7 were determined for all models as:

$$S = \frac{1}{n}\sqrt{\sum_{i=1}^{n}(V^E(\exp)_i - V^E(\text{cal})_i)^2} \quad (25)$$

Quaternary predictions using all models presented in Table 9 show good agreement with experimental data for this system. In this case, extracting information from the binary and ternary subsystems is meaningful. Results presented in Table 9 show that the new generation geometric model by Zhang[2] predicted quaternary experimental data better than others, whereas the Kohler model has the highest deviation.

CONCLUSIONS

The thermophysical properties are important to quantify the deviation from ideality of the thermodynamic functions of mixtures, which result essentially from molecular interactions. Multicomponent fluid systems rather than a single component are widely used in processing and product formulations in many industrial applications. Among the various properties considered in process and product design and optimization, these properties are of special interest. With this aim, densities and excess molar volumes V_m^E of binary and ternary and quaternary mixtures consist of 1-chlorobutane (1), butylamine (2), butyl acetate (3), and isobutanol (4) were measured at 298.15 K over a wide range of composition. Some geometric and empirical models have been extended to estimate the physicochemical properties of multicomponent systems based on the data of their subsystems. The measured data and calculated values of all systems are in good accordance and are theoretically and statistically satisfying.

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REFERENCES

(1) Li, R. Q. Semi-Empirical Methods For Predicting Thermodynamic Properties of Quaternary and Higher Order Systems. *CALPHAD* **1989**, *13*, 61–65.

(2) Zhang, G. H.; Wang, L. J.; Chou, K. C. A Comparison of Different Geometrical Models in Calculating Physicochemical Properties of Quaternary Systems. *CALPHAD* **2010**, *34*, 504–509.

(3) Iloukhani, H.; Khanlarzadeh, K. Volumetric Properties for Binary and Ternary Systems Consist of 1-Chlorobutane, n-Butylamine and Isobutanol at 298.15 K and Ambient Pressure with Application of the Prigogine—Flory—Patterson Theory (PFP) and ERAS-Model. *Thermochim. Acta* **2010**, *502*, 77–84.

(4) Khanlarzadeh, K.; Iloukhani, H. Application of ERAS-Model and Prigogine—Flory—Patterson Theory to Excess Molar Volumes for Ternary Mixtures of 2-Chlorobutane (1) + Butylacetate (2) + Isobutanol (3) at T = 298.15 K. *J. Chem. Thermodyn.* **2011**, *43*, 1583–1590.

(5) Iloukhani, H.; Khanlarzadeh, K. Densities, Viscosities, and Refractive Indices for Binary and Ternary Mixtures of N,N-Dimethylacetamide (1) + 2-Methylbutan-2-ol (2) + Ethyl Acetate (3) at 298.15 K for the Liquid Region and at Ambient Pressure. *J. Chem. Eng. Data* **2006**, *51*, 1226–1231.

(6) Fattahi, M.; Iloukhani, H. Excess Molar Volume, Viscosity, and Refractive Index Study for the Ternary Mixture {2-methyl-2-butanol (1) + tetrahydrofuran (2) + propylamine (3)} at Different Temperatures. Application of the ERAS-Model and Peng—Robinson—Stryjek—Vera Equation of State. *J. Chem. Thermodyn.* **2010**, *42*, 1335–1345.

(7) Redlich, O. J.; Kister, A. T. Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* **1948**, *40*, 345–348.

(8) Cibulka, I. Estimation of the Excess Volume and Density of Nonelectrolytes from Binary Data. *Collect. Czech. Commun.* **1982**, *47*, 1414–1419.

(9) Patterson, D.; Delmas, G. Corresponding States Theories and Liquid Models. *Discuss. Faraday Soc.* **1970**, *49*, 98–105.

(10) Prigogine, I. *The Molecular Theory of Solution*; North Holland: Amsterdam, 1957.

(11) Flory, P. J. Statistical Thermodynamics of Liquid Mixtures. *J. Am. Chem. Soc.* **1965**, *87*, 1833–1838.

(12) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents, Physical Properties and Methods of Purification*, 4th ed.; John Wiley & Sons: New York, 1986.

(13) Anton Paar digital densimeter. *Instruction Hand Book*; Anton Paar: Graz, Austria, 2002.

(14) Alberty, R. A.; Silbey R. J. *Physical Chemistry*, 1st ed.; Wiley: New York, 1992.

(15) Hui-Wen, C.; Chein-Hsiun, T. Densities, viscosities, and refractive indices for binary and ternary mixtures of acetone, ethanol, and 2,2,4-trimethylpentane. *J. Chem. Eng. Data* **2005**, *50*, 1262–1269.